ORIGINAL PAPER

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The effect of thermal pretreatment on the electrochemical response for palladium in aqueous media

Abstract Previous work on the electrochemistry of palladium in aqueous acid solution demonstrated the existence of two multilayer hydrous oxide reduction peaks, one at ca. 0.24 V and another at ca. 0.55 V vs. RHE, plus the presence of a reversible active surface state transition at ca. 0.24 V. In the present work with thermally activated palladium it was observed that, in agreement with the hydrous oxide reduction behaviour of the system, there is a second active state transition at $E{\geq}$ca. 0.45 V. In most of its reactions in aqueous acid solution, apart from its unusual capacity to absorb hydrogen, palladium exhibits properties very similar to those of platinum; however, palladium seems to be more prone to dissolution and subsurface oxygen formation. Also the premonolayer oxidation responses of these two metals are often different as the more active state of the palladium surface is not as readily generated as that of platinum. The electrocatalytic properties of palladium, as reported earlier, correlate quite well with the hydrous oxide and premonolayer oxidation behaviour of this electrode system.

Keywords Palladium · Thermal activation · Active surface states · Premonolayer oxidation · Electrocatalysis

Introduction

Recent work in this laboratory [1, 2, 3, 4] has highlighted the fact that surface metal atom activity is an important variable, both with regard to the electrochemical responses and electrocatalytic behaviour, of solid metal electrodes. Two widely ignored features are involved, active (or defect) states of metal surfaces and hydrous metal oxides [5]; the combined role of such species in many electrocatalytic processes was also discussed recently [2, 6]. The vital role of disorder or surface heterogeneity is now also an acknowledged feature in heterogeneous catalysis [7, 8]; high reactivity (or high turnover numbers) is often confined to metastable active sites [9] which in some cases appear to be single, highly active [3, 4, 10] protruding metal atoms, i.e. adatoms.

It is difficult to investigate rough surfaces [7] or highly active, discrete, surface metal atoms. The states involved are metastable (this was pointed out specifically by Taylor [9]), they tend to decay spontaneously, are not easily reactivated and there are not many techniques available for measuring the energy values and coverage of these unstable species. Conventional electrochemical techniques, e.g. cyclic voltammetry, are useful as they may be used to generate active states of surfaces [3, 11] and provide, in terms of redox potentials and peak charges, an indication of the activity and coverage of the unusual species involved.

The study of highly active surface states at a practical level is obviously difficult as such states are neither well defined nor stable. Significant overlap with this active surface state area is found in the case of metal microcluster chemistry [12]; active non-equilibrium states of metals and unusual redox behaviour are common to both areas. The electrochemical responses of active gold [3, 13, 14], platinum [1, 4] and copper [2, 15] surfaces in aqueous media were described recently.

The present work is concerned with palladium in aqueous, mainly acid, solution. Previous work in this laboratory on the electrode system in question has been concerned with monolayer (or α) oxide [16, 17] and multilayer (or β) oxide [11, 17, 18, 19, 20] growth, electrocatalysis [21] and surface activation or disruption [11]; the technique used for the last [11] was repeated growth and reduction of multilayer oxide films (references to the work of many other authors in the palladium area are given in these earlier publications and an account of the conventional electrochemistry of palla-

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dium is provided by Woods [22]). In the present case, a different activation technique, involving rather severe thermal pretreatment of palladium in an inert gas atmosphere, was employed. This approach was used recently with platinum [1, 4] and it is interesting to compare the behaviour of these two metals, which occur in the same group of the Periodic Table; their chemical and electrochemical properties should, therefore, be rather similar. Palladium seems to be somewhat more susceptible to dissolution in acid media [23] and its ability to absorb large quantities of hydrogen at ca. 0.05 V vs. RHE is very well known [24].

Experimental

The equipment and techniques used in the present investigation were described earlier [1]. While much of the early work in this project was carried out with a cell operated at room temperature (20 °C), later work at elevated solution temperature involved suspending the electrochemical cell and reference electrode compartment in a water bath in which the temperature was controlled electronically (± 0.1 °C) at the desired value. The loop of palladium wire (ca. 20 cm long, 0.5 mm diameter, Johnson Matthey, Puratronic grade) was thermally pretreated by heating it electrically (8–10 A, typically for 25 s) in an argon atmosphere within the cell (the 5% H_2 in N_2 gas mixture employed earlier with platinum [4] was not used in this case to avoid complications due to absorbed H_2) and, after the system had cooled, the deoxygenated electrolyte was added to the cell and cyclic voltammetry measurements were carried out, usually without further electrode pretreatment. The electrolyte solutions were made up using triply distilled water and Analar grade H_2SO_4 or NaOH. All connections to the cell (including the flat-flanged lid) were of ground glass and the pressure of argon within the cell was maintained at a slightly elevated pressure to prevent entry of oxygen. The cell was fitted with a carbon counter electrode (Alfa Aesor, Ultra "F" purity, 7.7 mm diameter) and a hydrogen ($p = 1.0$ atm) reference electrode in the same solution. Most of the responses shown here correspond to the first cycle, commencing with the positive sweep; to avoid substantial absorption of hydrogen by the metal, the lower limit was restricted to $E \geq 0.15$ V. All experiments were repeated at least once to ensure that the observed trends were reasonably reproducible.

Attention is drawn here to one aspect of the thermal pretreatment process and the unusual voltammetric responses observed after the same. The highly active (or superactive) surface state, which as demonstrated by recent SEM and AFM work with gold [13, 14] is of ill-defined, rough or disordered character, is usually not obtained after one short heat pretreatment with a fresh sample of wire. To observe unusual responses it was usually necessary to repeat the heat pretreatment several times in the case of both gold and palladium, more so in the case of platinum (intermediate periods of severe cathodization, which induce hydrogen embrittlement of the metal surface [3, 14], appear to be of benefit with regard to achieving the superactive state of platinum). Once the superactive state is achieved with an electrode, it is not readily lost (any decay of activity is then usually restored by a single heat pretreatment). It seems that the attainment of the superactive state requires the development of a disordered microstructure in the outer layers of the metal lattice, and this is initially difficult to achieve (the state in question is clearly metastable). The induced changes are obviously not a matter of surface contamination by impurities; the same type of unusual states or responses may be achieved by cathodic pretreatment [3, 25] or (in the case of palladium) by repeated growth and reduction of multilayer oxide films [11]; furthermore, these active state responses correlate quite well with electrocatalytic behaviour. As outlined earlier for platinum [4], and demonstrated here later for palladium, anomalous electro-chemical responses after thermal pretreatment tend to be far more dramatic or obvious at elevated cell temperatures.

Results

Effect of thermal activation of palladium on the voltammetric response for acid solution at room temperature

A typical voltammogram for a conventional bright palladium electrode in acid solution is shown in Fig. 1a. The anodic current over the range 0.2–0.5 V, with a broad maximum at ca. 0.28 V, may include contributions due to adsorbed hydrogen removal, double layer charging and hydrous oxide formation (the response due to the latter reaction, i.e. premonolayer oxidation, is assumed to be the dominant feature over this range in some of the later cyclic voltammograms presented here). The conventional double layer response, as virtually the sole anodic feature, extended in this case over the range 0.5–0.9 V. The gradual increase in anodic current above the latter value is assumed to be due to monolayer (α) oxide formation and the reduction of this film gave rise
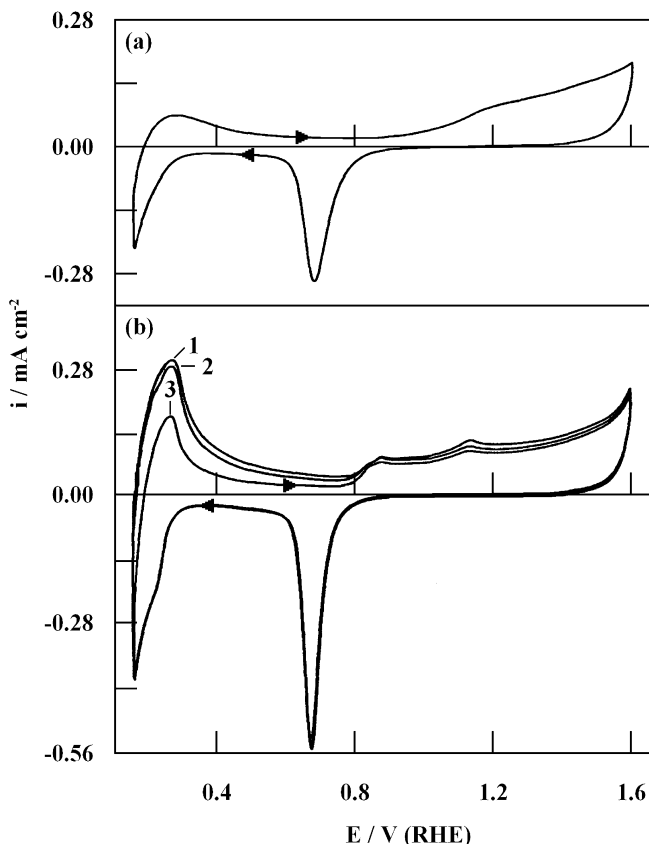

Fig. 1 Cyclic voltammograms (0.15→1.60 V, 50 mV s^{-1}) for a polycrystalline palladium electrode in 1.0 mol dm^{-3} H_2SO_4 at 20 °C: (**a**) unheated wire; (**b**) thermally pretreated wire (8 A, 1090 °C, for 25 s); in the latter case the first three successive cycles are shown

to the well-defined cathodic peak at ca. 0.68 V in the subsequent negative sweep.

Some points are worth noting here: (1) the increase in current at the beginning of the α oxide region was quite gradual (this is attributed to the low energy state of most of the surface metal atoms); (2) a substantial increase in slope of the α oxide region is evident at ca. 1.1 V (in later work with more active palladium surfaces a small peak was observed in this region); (3) the charge in the α oxide formation region generally exceeded that for the corresponding oxide reduction peak (there may be various contributions to this inequality, e.g. some palladium dissolution above 1.1 V [23], formation of subsurface oxygen [26] whose subsequent reduction is sluggish, formation of some (β) oxide species whose reduction occurs rapidly, as outlined earlier [11], only at low potentials). The increase in cathodic current below 0.3 V in the negative sweep may be due to a combination of two factors: reduction of residual hydrous oxide species (and perhaps subsurface oxygen), plus formation of adsorbed (and possibly some absorbed) hydrogen.

Heat treatment of the palladium wire in an inert gas atmosphere at 1090 °C resulted in substantial changes in the voltammetric response (Fig. 1b). These changes were gradual in that they became more marked as the number of heat pretreatments for a given sample was increased. This effect is not too surprising; the activation process does not yield a surface of well-defined structure. Instead (as demonstrated earlier by SEM and AFM studies of thermally pretreated gold [13]), the activated surfaces tend to be of a quite disordered, metastable character. The changes in the nature of the response on repeated heating and cooling may be due to two factors: (1) a reduction in surface grain size, accompanied by an increase in surface area, and (2) a reduction in the lattice stabilization energy of surface palladium atoms. Usually the voltammetric response in the α oxide formation region was sharper, or more clearly defined, with thermally pretreated electrodes.

The onset of the monolayer oxide formation reaction in Fig. 1b, at ca. 0.8 V, is much more obvious as compared with Fig. 1a. Indeed, the potential in question virtually coincides with that for the onset of monolayer oxide reduction in the negative sweep. Both processes in this region involve relatively active palladium atoms (Pd*), in the anodic case as reactants and in the cathodic case as products; the common reaction may be represented as follows, viz.:

$$Pd^* + H_2O \underset{cathodic}{\overset{anodic}{\rightleftarrows}} PdO + 2H^+ + 2e^- \quad E \approx 0.8 \text{ V} \quad (1)$$
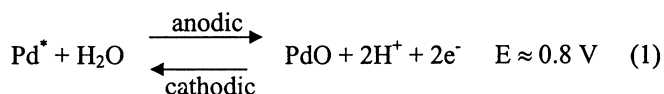
The plateau in the case of the anodic response may be attributed to a combination of several effects, e.g. a progressive reduction in the level of activity of the remaining surface metal atoms, a progressive reduction in the ease of access to those metal atoms remaining unoxidized (the oxidation of the more active sites impeding access to the less active remaining ones) and the usual type of dipole-dipole ($Pd^{\delta+}$-$OH^{\delta-}$) repulsion effects (resulting in place exchange, etc. [27]) at the interface. The cathodic response is sharper as access is not a problem and the product metal atoms do not mutually repel one another; the peak maximum is at a slightly negative value (compared with the onset potential) as it corresponds to a high (but transient) coverage of rather active, nascent, metal atoms. The appearance of the anodic peak, at ca. 1.13 V, in the α oxide formation region is worth noting. It is obviously a rather minor feature compared with the overall α oxide formation response, the reaction involved [possibly $Pd(OH)_4$ formation] evidently being restricted to special sites [probably where PdO or $Pd(OH)_2$ groups protrude above the α oxide surface]. Similar behaviour, i.e. anodic peaks in the oxide film region, is well known for other electrode systems; it has been attributed, e.g. in the case of RuO_2 anodes in base [28], to an increase in the extent of oxidation of reactive oxycation species at the interface {the Ni(II)/Ni(III) reaction in oxide films on nickel in base [5] is a further example of such behaviour}. According to Pourbaix [29], the standard electrode potential for the $Pd(OH)_2$/$Pd(OH)_4$ transition is ca. 1.28 V vs. RHE at 25 °C. Hence the anodic feature in the positive sweep in both Fig. 1b and Fig. 2 at ca. 1.1 V may be due to Pd(II) to Pd(IV) conversion at a limited number of surface oxide sites (the precise value of the transition potential is probably affected by the fact that reacting species are
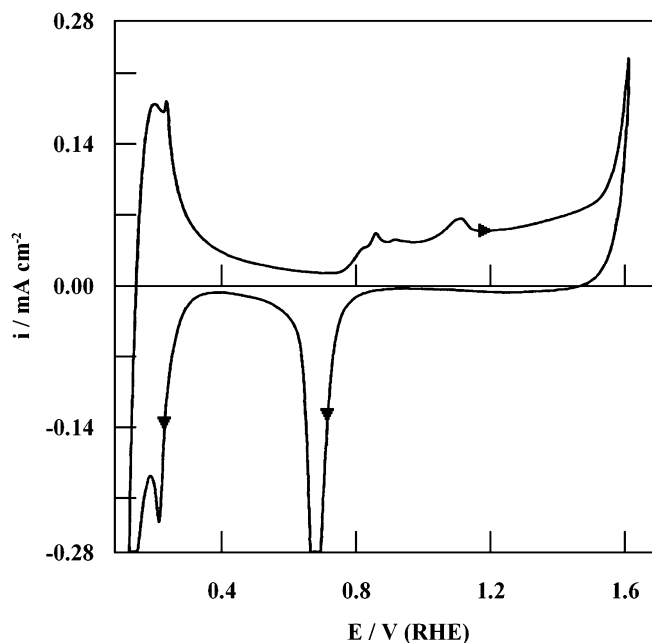

Fig. 2 Cyclic voltammogram (0.15→1.6 V, 10 mV s^{-1}) for a polycrystalline palladium electrode in 1.0 mol dm^{-3} H$_2$SO$_4$ at 20 °C; the wire in this case has been subjected to several earlier thermal pretreatments (1090 °C for 25 s); note the reversible transition, described earlier [11], at ca. 0.24 V

not present at the interface under standard state conditions).

A further interesting feature in Fig. 1b is the change in slope in the hydrogen adsorption response in the negative sweep at ca. 0.22 V. This may appear trivial, but with an electrode subjected to a more extensive series of heat pretreatments (Fig. 2), a distinct cathodic peak, with a corresponding anodic counterpart in the positive sweep, appeared in this region. The response in question was quite small; it was superimposed on a large background response and was most clearly evident at slow sweep rates, e.g. 10 mV s^{-1} in Fig. 2. The reversible response was observed earlier [11] with palladium electrodes in acid solutions which were activated by repeated growth and reduction of multilayer hydrous oxide films. The feature in question was attributed to a highly active metal atom (Pd**)/β oxide [assumed to be a Pd(HO2) species] transition, viz.:

$$Pd^{**} + 6H_2O \longrightarrow \left[Pd(OH)_6\right]^{2-}_{ad} + 6H^+ + 4e^-$$
$$E = 0.24 \text{ (acid)} \tag{2}$$
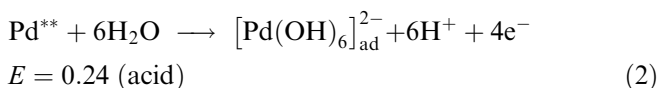
It appears that, as discussed earlier for platinum [1], there are different states of surface metal atom activity, with the occupancy or coverage of these states varying with the extent of activation or thermal pretreatment. With the initially unactivated surface the occupancy of state Pd* is very low and that of Pd** virtually negligible (the α oxide formation reaction of Fig. 1a is confined largely in this case to the region above ca. 1.0 V). With moderate activation, state Pd* becomes significantly occupied and oxidation commences at ca. 0.8 V (Fig. 1b). Finally, with further activation the occupancy of state Pd** becomes significant and a reversible response is observed at 0.24 V (Fig. 2). There may be other active state responses for this electrode system, e.g. there is often (as outlined later) a further premonolayer response at ca. 0.4 V. An indication of further complexity is evident at the beginning of the α oxide formation region in Fig. 2, where three small overlapping peaks ($E_{max} = 0.83$, 0.86 and 0.92 V) are evident; these peaks, which were even more obvious at lower sweep rates, e.g. 5 mV s^{-1}, are assumed to be due to reaction of palladium agglomerates of slightly different energy values.

A curious feature of the three successive scans shown in Fig. 1b is that while the cathodic current response in the negative sweeps remain almost invariant, the anodic current responses in the positive sweep undergo a substantial decrease on repeated cycling. Loss of absorbed hydrogen is considered an unlikely possibility as the lowest potential (0.15 V) was applied initially only at the beginning of the first cycle, i.e. there was little opportunity for absorption of hydrogen. The other possibility is some type of surface deactivation process, e.g. dissolution of very active palladium atoms as these undergo oxidation, or formation of either subsurface oxygen or some form of recalcitrant metal oxide species, i.e. one that is reluctant to undergo reduction. The invariant nature of the response in the negative sweep is assumed to reflect the fact that the process involved relates to the conventional, rather than the active state, behaviour of palladium, i.e. the rate of reduction of both the hydrous oxide and subsurface oxygen is relatively slow.

Effect of elevating the pretreatment temperature and cathodic pretreatment

The effect of thermal pretreatment at 1090 °C, as summarized in Fig. 1b, was not particularly dramatic [the regular monolayer response above ca. 0.8 V was more clearly defined and eventually a reversible feature emerged (Fig. 2) at ca. 0.24 V]. Increasing the pretreatment temperature to 1260 °C led to the emergence of a new anodic feature at ca. 0.7 V (see the arrow in the positive sweep in Fig. 3a); the response in question commenced at ca. 0.56 V, i.e. below the maximum for monolayer oxide reduction peak, and overlapped with the conventional monolayer oxide formation response, the onset of the latter giving rise to the increase in anodic current at ca. 0.79 V. There was also a minor shoulder
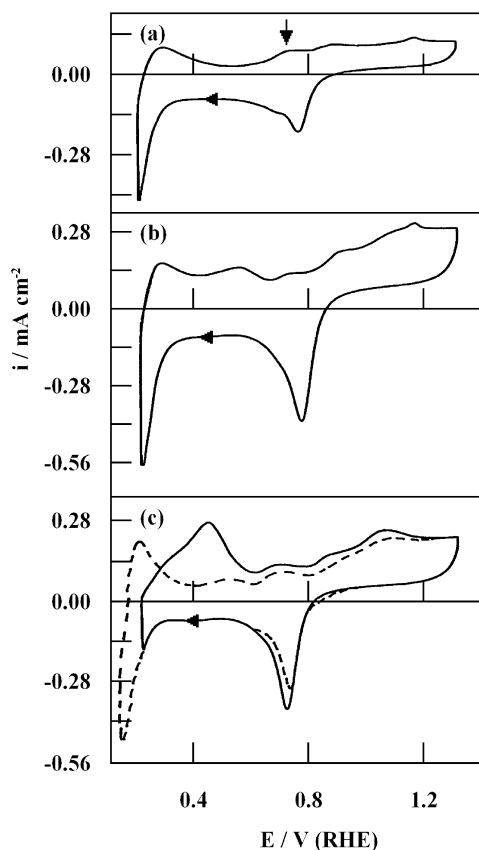

Fig. 3 Cyclic voltammograms (0.2→1.3 V, 50 mV s^{-1}) for a polycrystalline palladium wire electrode in 1.0 mol dm^{-3} H$_2$SO$_4$ at 20 °C; the wire was thermally pretreated at 10 A, 1260 °C, for 25 s: (a) no further pretreatment; (b) prepolarized at 0.15 V for 3 min; (c) prepolarized at 0.25 V for 3 min (the *dashed line* in this case shows a second sweep recorded from 0.15 to 1.3 V at 50 mV s^{-1})

on the negative side of the monolayer oxide reduction response.

As demonstrated earlier for platinum [1], the anomalous (or active state) responses for a thermally pretreated electrode may be further enhanced by cathodic pretreatment; the latter may be considered as a form of hydrogen embrittlement, as discussed recently for gold [3]. To minimize complications due to the presence of absorbed hydrogen, the polarization pretreatment with palladium was restricted to $E \geq 0.15$ V. The response recorded after polarizing the thermally pretreated electrode at 0.15 V is shown in Fig. 3b. A new feature, in the form of a small, rather broad peak, $E_{max} = 0.54$ V, was observed in the positive sweep; this feature has no distinct cathodic counterpart in the negative sweep.

Polarizing a similar, thermally pretreated, palladium electrode at 0.25 V, i.e. at a reduced hydrogen coverage or activity at the interface (compared with 0.15 V), resulted in a substantial enhancement of the response for the new anodic peak (E_{max} in this case was at ca. 0.43 V) (full line in Fig. 3c). This enhancement was not maintained in the second cycle (dashed line in Fig. 3c), the major anodic feature at low potentials in the latter case being the response at the initial stage ($E_{max} = 0.25$ V) of the positive sweep. Polarizing at higher potentials resulted in little enhancement of the anodic response at low potential. Maximum enhancement of this anodic feature just above 0.4 V was observed on polarization at 0.25 V; the latter value almost coincides with that for the reversible response noted earlier (Fig. 2) for the highly active state of palladium in acid. The peak just above ca. 0.4 V in Fig. 3b or Fig. 3c showed little sign of a cathodic counterpart, i.e. the process involved, at room temperature, is not very reversible.

Effect of elevating the solution temperature

As demonstrated earlier for platinum [4], elevating the solution temperature has a dramatic effect on surface active state, premonolayer oxidation, responses. The effect of increase in temperature was assumed to be twofold: (1) it enhances reaction rates; (2) it raises the percentage of active surface metal that can attain a higher energy state, i.e. as shown previously for Pt [4], the anodic responses at low potentials are the ones that are most enhanced. There is a tendency for the metastable active states to spontaneously decay (this is the basis of Ostwald ripening phenomena [30]). This trend is counteracted by raising the solution temperature which promotes the formation, or increases the coverage, of highly active, relatively mobile surface metal atoms (or adatoms) which often appear to be the transient species involved in both premonolayer oxidation and active site behaviour [2, 6] at metal/solution interfaces.

Typical responses for palladium, before and after thermal pretreatment of the latter, in acid solution at 35 °C are shown in Fig. 4. The most unusual feature is the appearance of the two anodic peaks (A and B) at the

beginning of the positive sweep in Fig. 4b. The peak maximum values, 0.24 and 0.41 V, coincide quite closely with those reported earlier [11] for the reduction of Pd(HO2) and Pd(HO1) components in multilayer Pd hydrous oxide deposits. It is assumed that the repeated thermal pretreatment yielded significant coverage of active palladium atoms of two distinguishable types, one of which is converted on oxidation to Pd(HO2) and the other to Pd(HO1) oxides, giving rise to peaks A and B, respectively. The second peak was rather broad and there was significant background anodic current between these two peaks. The reversibility of these premonolayer oxidation responses was rather poor (such behaviour was noted earlier for both gold [3] and platinum [4]), but there was a significant increase in cathodic current in the negative sweep below 0.5 V. The onset of monolayer oxidation in the positive sweep, at ca. 0.8 V, was again much more obvious in the case of the thermally pretreated electrode.

Typical examples of the first and second cycle responses for a thermally pretreated palladium electrode in acid solution at 60 °C are shown in Fig. 5. In the first cycle, peak B was the dominant premonolayer oxidation response while peak A was quite small. However, in the second cycle the first anodic peak was the main feature in this region. There was no sign of a cathodic response in the peak B (or HO1) region of the negative sweep, but a substantial increase in current was observed below 0.3 V. A further feature noted in some instances at elevated temperature ($T \geq 50$ °C) was the appearance of a small, approximately constant, anodic current over the upper region (from ca. 1.4 to ca. 0.8 V) of the negative sweep. This is assumed to be due to slight dissolution of
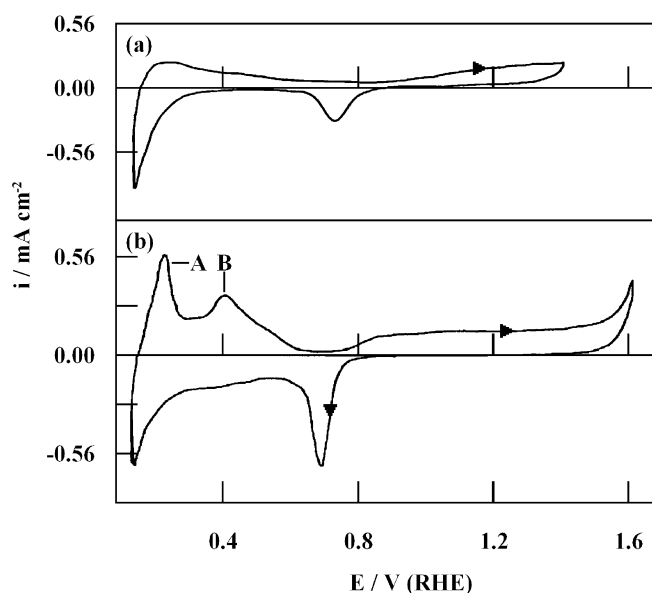

Fig. 4 Cyclic voltammograms for palladium (50 mV s^{-1}) in 1.0 mol dm^{-3} H$_2$SO$_4$ at 35 °C: (a) unheated wire electrode (0.15→1.4 V); (b) thermally pretreated (1260 °C for 25 s) electrode (0.15→1.6 V)

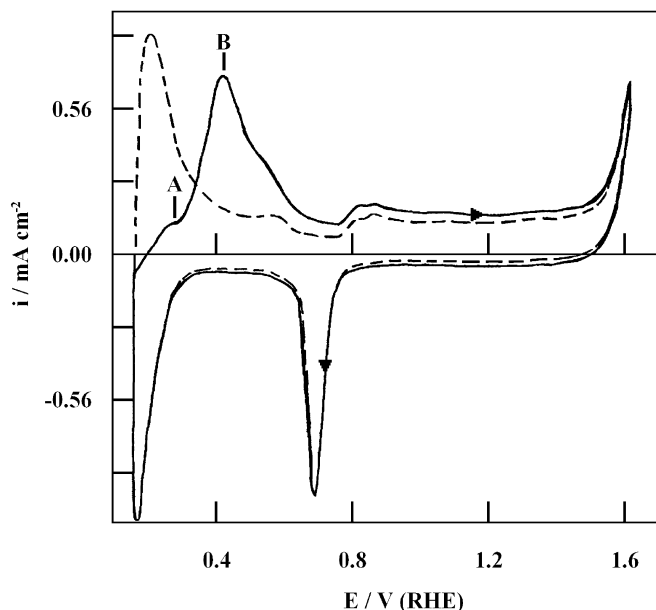**Fig. 5** Cyclic voltammogram (0.15→1.6 V, 50 mV s^{-1}) for a thermally activated (1260 °C for 25 s) palladium wire electrode in 1.0 mol dm^{-3} H$_2$SO$_4$ at 60 °C; both first (*full line*) and second (*dashed line*) sweeps are shown

Fig. 6 Cyclic voltammograms (0.15→1.3 V, 50 mV s^{-1}) for a thermally activated (1260 °C for 25 s) palladium wire electrode in (a) 1.0 mol dm^{-3} H$_2$SO$_4$ at 80 °C and (b) 1.0 mol dm^{-3} NaOH solution at 80 °C (*full line*) and 20 °C (*dashed line*; the range for the latter was 0.20–1.30 V)

palladium; to reduce the impact of the latter, most of the voltammetry responses at higher temperature, e.g. 80 °C, were recorded using a reduced upper limit, e.g. 1.30 V.

Responses for thermally pretreated palladium in aqueous acid and base at 80 °C are shown in Fig. 6. The overall response in acid (Fig. 6a) may be subdivided into two regions: 0.15 to ca. 0.7 V, premonolayer oxidation; ca. 0.7 to 1.3 V, monolayer oxidation. In some cases, peak A, at ca. 0.2 V, was quite small but had a cathodic counterpart at ca. 0.16 V. Peak B had a maximum at ca. 0.34 V; it was usually quite broad with a number of distinctive features at more positive potentials, e.g. there is a reversible feature at ca. 0.41 V that is reminiscent of the "butterfly peaks" response reported for single-crystal electrode surfaces [31]. In this case also the anodic charge in the α oxide formation region significantly exceeded the cathodic charge for the corresponding reduction peak; the anodic charge for peak B or HO1 formation generally exceeded that for its cathodic equivalent in the negative sweep, but it is obvious in this case that anodic peak B does indeed have a cathodic counterpart (of lower magnitude).

The response for the same thermally activated electrode in base at 80 °C (full line in Fig. 6b) is quite different to that observed for palladium in acid. With base there was no premonolayer oxidation response at elevated temperature; the current, even in the positive sweep, remained cathodic until ca. 0.6 V. Evidently most of the active surface palladium atoms undergo oxidation when the electrode is immersed in base, the stability of the product [Pd(OH)$_6$]$^{2-}$ species being significantly in-

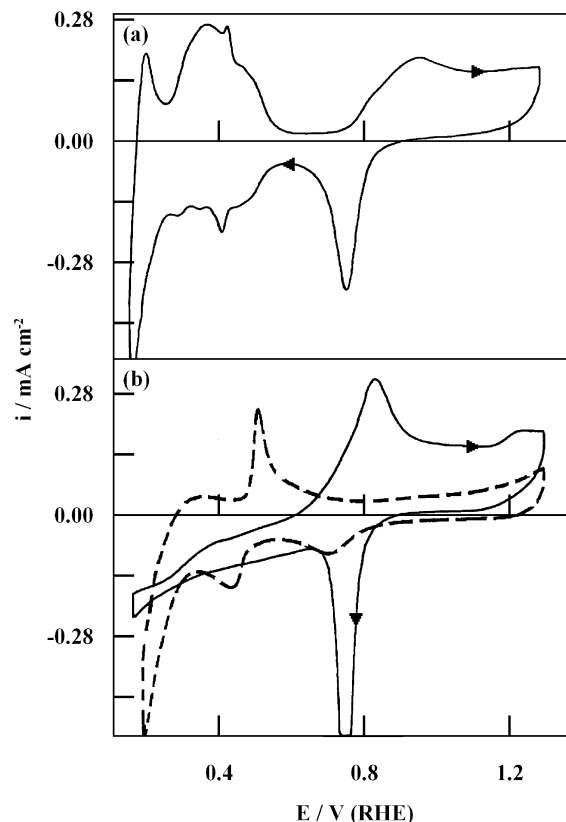creased at high pH owing to the super-Nernstian E/pH shift [32]. The latter interpretation requires some qualification: the increased stability is only with respect to reduction of these palladate species to the highly active state of the metal (Pd**); the deposit is still unstable in base with respect to a less active state of palladium; this explains the relatively low cathodic response in base below 0.6 V.

While the premonolayer oxidation behaviour of palladium in acid is rather similar to that of platinum [1, 4], some significant differences were noted. For example, with activated platinum in acid at elevated temperature [4] the predominant voltammetric response occurred at 0.25 V and is assumed to involve the HO2 oxide. However, with activated palladium in acid at 80 °C (Fig. 6a) the predominant feature at low potential was peak B, close to 0.4 V, which indicates the involvement of HO1 species (the anodic response in this region is also evident in other diagrams shown here). However, the anodic peak in question (B in Fig. 6a) commenced at ca. 0.25 V and hence the initial product in this region may be of intermediate character (containing elements of HO1 and HO2). Attention is drawn to such behaviour here because with platinum the super-Nernstian E/pH

shift appears to be confined to Pt(HO2) hydrous oxide deposits [33]; Pt(HO1) exhibits conventional oxide behaviour. Even with activated palladium the unusual E/pH response (or shift) is not observed on switching from acid to base at room temperature. As outlined by the dashed line in Fig. 6b, there was no extended cathodic response at the lower end of the positive sweep recorded at the lower temperature. This discrepancy, i.e. the absence of the super-Nernstian shift with palladium at room temperature, will be discussed in more detail elsewhere (Burke LD, Nagle LC, to be published); the effect may be attributed to the difficulty in generating (or the lack of stability) of the HO2 precursor state of palladium. Such a state is more easily achieved with platinum [1, 4], but for both metals the state in question is quite unstable from a thermodynamic viewpoint; hence complex behaviour is not very surprising.

Discussion

The electrochemical behaviour of palladium in acid solution (apart from the hydrogen absorption behaviour which is ignored here) is quite similar to that of platinum. This is true not only with regard to the conventional response (Fig. 1), but also in terms of multilayer hydrous oxide reduction behaviour. The latter was outlined recently for palladium in acid [11]; two major cathodic responses were observed, one at ca. 0.55 V and another at ca. 0.24 V, corresponding to the reduction of hydrous oxide components HO1 and HO2, respectively (similar hydrous oxide reduction behaviour was reported earlier [34] for platinum in acid solution). It was suggested [11] that the reversible transition at 0.24 V in Fig. 2 is due to an active palladium/HO2 oxide transition (in the earlier work, involving electrochemical activation, the background responses were relatively low, the sharp peaks at 0.24 V were more evident and were shown, in terms of the charge values involved, to be directly related to the prior multilayer HO2 reduction response recorded during the activation stage).

It is assumed that all surface metal atoms are more active than their bulk equivalents as the former have a lower lattice stabilization energy. However, the surface atoms will spontaneously tend to lose this excess energy by increasing their lattice coordination number and lattice stabilization energy, as far as this is possible. Bulk palladium is expected to undergo oxidation at ca. 0.9 V [29] and, in the case of Fig. 1b and Fig. 2, monolayer oxide formation commences at ca. 0.8 V, the lower value in the latter case reflecting the slightly higher activity of the surface, as compared with bulk, metal atoms. The onset of oxidation is less obvious in Fig. 1a; however, the latter response is for a relaxed, low-energy surface which had little prior activation pretreatment. The low anodic response over the range 0.8–1.1 V in Fig. 1a may be attributed to the presence of impurities. However, we

considered this as unlikely; the monolayer formation response of bright palladium did not alter appreciably over several cycles, even though it is usually assumed that formation and reduction of a monolayer oxide deposit (the upper limit involved here is 1.6 V) is an effective method for desorbing or destroying surface contaminants on an active electrode surface.

The variation of oxidation behaviour within the monolayer oxide region may be rationalized in terms of a surface grain size effect. When the grain size is exceptionally small, quantum confinement effects operate (this is the basis of superactivation) and oxidation occurs within the double layer region. However, it is clear from Henglein's work [12] that for such a shift in potential to occur to a significant degree, the number of atoms per particle must be exceptionally small, possibly $n < 10$. This means that there is an intermediate particle size range, e.g. $10 < n < 1000$, in which the metal activity is at an intermediate level (not quite superactive but greater than that of an average surface atom). Such atoms at the surface of particles of intermediate size or activity are assumed to undergo oxidation at the early stages of the monolayer oxide region. Such behaviour, a marked response or peak at the start of the monolayer oxide formation region, was pointed out recently for gold (see Fig. 7 in [3]). On elevating the solution temperature, a peak emerged at the beginning of this region in the case of cathodically activated gold in acid [3] and there are also indications of such discrete anodic peak behaviour just above 0.8 V (positive sweep) in the responses shown here in Fig. 1b and Fig. 2. It is worth noting also that variation in surface metal atom activity need not be considered solely on the basis of the particle size effect (the latter model is convenient as it related to Henglein's microcluster data [12]); however, anomalously high metal atom activity has also been attributed [35] to the presence of extended defects, i.e. a very high surface density of the latter (which may be regarded as the equivalent of an interconnected surface microparticle state) is also one of high activity. Again it is stressed that such a state is unstable and will gradually revert to a more stable form. The latter state is probably the dominant one for the palladium wire in the first instance (as manufactured or delivered). There is considerable expenditure of energy (mainly in this case in electrical form) in changing the response from that in Fig. 1a to that in Fig. 1b or Fig. 2; the difference is attributed mainly to a change in both surface microstructure and energy.

Two other complications that require attention in the case of palladium (and perhaps all noble metals) are: (1) the formation or existence of subsurface oxygen, and (2) the generation, even in the monolayer (α) oxide region, of hydrous (β) oxide species. The presence of subsurface oxygen in palladium, pretreated electrochemically [26] or exposed to a gaseous oxidizing environment [36], has been established by surface analytical techniques and such oxygen can apparently participate in catalytic reactions, e.g. CO oxidation [36], at the metal surface.

Hydrous oxide species usually only undergo reduction at low potentials (note the inflection in the cathodic peak at ca. 0.24 V, i.e. in the HO2 reduction region, in the negative sweep in Fig. 1b and Fig. 2). These two side reactions explain the discrepancy in charge values between the α oxide formation and reduction responses, e.g. in Fig. 1b.

Raising the thermal activation temperature of the palladium to 1260 °C (Fig. 3a) resulted in the appearance of a rather broad peak at ca. 0.7 V in the positive sweep, i.e. just prior to the onset of monolayer oxide formation (plus an indication of a corresponding cathodic feature on the subsequent negative sweep). This novel anodic peak corresponds quite closely to the state (b) response postulated earlier [1] for platinum in acid. When the palladium electrode, after thermal activation at 1260 °C, was subjected to additional cathodic pretreatment (Fig. 3b), the anodic peak at 0.7 V was retained but was now accompanied by a further peak at 0.55 V. This latter feature is assumed to correspond to an active palladium/HO1 transition, i.e. the equivalent of the state (c) response outlined earlier for platinum [1]. This anodic response at ca. 0.55 V was further enhanced by either polarizing at 0.25 V (apparently an optimum value; Fig. 3c) at 20 °C or by raising the cell operating temperature to 35 °C (Fig. 4b). The peak maximum value for the latter case was slightly lower, ca. 0.4 V, and it is not clear whether this is due to the existence of two separate transitions (one at 0.55 V and the other at 0.4 V; see Fig. 6a) or a slight variation in the nature of the species involved in the transition.

The optimum response at 0.45 V on polarization of the thermally pretreated palladium electrode at 0.25 V (Fig. 3c) is interesting as the polarization value is quite close to the peak for HO2 formation (Fig. 2). It may be that if the very active palladium atoms (Pd**) are removed, via HO2 formation, the coverage of less active (Pd*) atoms, which yield the HO1 formation response, is consequently enhanced. It is also assumed that polarizing above 0.25 V does not enhance the surface activity due to low pressure of hydrogen at the interface (cathodic activation [3] is assumed to be a hydrogen embrittlement effect).

The other marked feature in Fig. 4b is the appearance of anodic peak A at 0.24 V; this response is attributed to an active Pd**/HO2 oxide transition. There was little indication in this case of hydrous oxide reduction peaks in the negative sweep, but there was a substantial flow of cathodic current below 0.6 V. Similar behaviour was reported earlier for both superactivated platinum [4] and gold [3]; it is not totally clear why in some cases the cathodic responses in all three systems are sluggish. At a cell temperature of 60 °C (Fig. 5) the predominant feature in the first positive sweep is peak B at ca. 0.45 V; peak A was quite small and there was a hint of a shoulder at ca. 0.55 V. This latter feature is more distinct in the second cycle in which peak B is absent, being replaced later by a marked anodic response at ca. 0.2 V;

the latter is assumed to involve very largely HO2 formation.

It is assumed here that peaks A and B in Fig. 5 reflect premonolayer oxidation responses; since B occurs at a more positive potential it evidently reflects the reaction of less active palladium atoms than those involved in peak A. It is assumed that in the course of palladium activation at 1260 °C the palladium atoms are reasonably mobile, but they lose this mobility when the heating current is switched off and the sample cools. However, cooling is not instantaneous; some thermal annealing occurs, e.g. the surface metal clusters increase in size, the defect density drops and the mean activity of palladium atoms at the surface decreases. Hence, in the first positive sweep (Fig. 5), most of the palladium atoms are at a moderate level of activity and they undergo oxidation at ca. 0.45 V to yield HO1 oxide species.

To form HO2 oxide the surface Pd atoms must be unusually active and this state is not readily achieved by thermal pretreatment. The higher energy state in question may be attained by room temperature activation procedures which do not entail the post-activation annealing stage. It is worth noting that in the earlier work with superactive palladium surfaces [11], which involved room temperature electrochemical activation, the active state redox transition was observed almost invariably at ca. 0.24 V. It seems that in the case of Fig. 5 the first cycle after thermal activation resulted in HO1 formation (peak B, at ca. 0.45 V). On the second cycle (dashed line in Fig. 5), peak B was absent; peak A (attributed mainly to HO2 formation) was the predominant premonolayer oxidation response in this case. Evidently the oxide formation/reduction response associated with the first cycle resulted in a major increase in both the energy and the coverage of highly active palladium atoms at the interface; hence the marked HO2-type response.

The most obvious demonstration of two distinct types of redox behaviour for a palladium surface in acid solution is the result shown for 80 °C (Fig. 6a). The conventional monolayer oxide response commences above ca. 0.75 V and the reduction of this deposit exhibits the usual hysteresis. The discrepancy between the anodic and cathodic charge in this region is again evident, but there is quite a significant flow of cathodic current towards the end of the negative sweep; this feature is attributed mainly to a combination of hydrous (HO2) oxide and subsurface oxygen reduction. The response for the oxidation of superactive platinum, between ca. 0.2 to 0.55 V, is more marked in this case; the charge involved is on a par with that associated with the monolayer oxide formation process; there is clearly a strong element of reversibility in the premonolayer oxidation response at 80 °C.

The unusual type of response observed for superactive palladium at 80 °C in base (Fig. 6b) is quite similar to that reported earlier for platinum (see Fig. 8 in [4]). Such behaviour has been explained earlier [32] in terms of a super-Nernstian E/pH shift. An interesting feature

is that such behaviour is not usually observed at lower temperature; in the case of platinum, only the HO2 oxide exhibits a super-Nernstian E/pH shift [33]; the HO1 oxide of platinum exhibits regular oxide behaviour, i.e. the Pt(HO1) oxide response (and apparently its Pd equivalent) exhibits a pH-independent shift, in terms of the RHE scale, on altering the solution pH. Further evidence to support this viewpoint, and in particular the difficult of forming the HO2, as opposed to the HO1, oxide on palladium, will be provided shortly (Burke LD, Nagle LC, to be published).

According to the IHOAM model of electrocatalysis [2], even unactivated palladium surfaces contain a very low coverage of superactive palladium atoms at active surface sites [9]. These atoms undergo oxidation to yield incipient hydrous oxide species, which in turn mediate the oxidation of dissolved reductants within the double layer region (since it magnifies or amplifies the active site response, catalytic responses are often a useful indicator of active site behaviour). In the presence of hydrazine in acid [21] a palladium black electrode yields a major anodic response just above 0.25 V (supporting the notion of a HO2 mediator), whereas with bright palladium the same type of increase commences only above ca. 0.45 V (suggesting the involvement of a HO1 mediator at the less active surface). The palladium black electrode is intrinsically more disordered or active and thus the involvement of the more active Pd(HO2) precursor state in the case of such electrodes is not an unreasonable assumption. With palladium in base [21] the same reaction commences at a lower potential of ca. 0.20 V, and is independent of the state of the surface (similar behaviour, a lower onset potential for hydrazine oxidation in base as compared with acid, was outlined earlier [37] for Pt).

Palladium seems to be less active from an electrocatalytic viewpoint than platinum [21]. For both metals the region of high catalytic activity is often predominantly the double layer region where adatom/hydrous oxide transitions occur without interference from the monolayer oxide deposit. From an electrocatalytic reduction viewpoint, dichromate and persulfate reduction on bright Pd in acid [21] exhibit interesting behaviour. Both reactions exhibit a severe drop on rate as the potential is increased above ca. 0.45 V; evidently the reaction mediator (Pd*) is lost due to Pd(HO1) formation in this region. For both reactions the catalytic function is totally lost with regard to the reductions below 0.8 V, i.e. the loss of activity is due to disappearance of the Pd* mediator, and not the formation of the monolayer oxide film.

Premonolayer oxidation responses provide strong support for the existence of active states of surface metal atoms. However, peak potential values in this area, even where the responses appear to occur in a reasonably reversible manner, need to be interpreted with a degree of caution. They probably relate, in terms of charge, to all metal atoms capable of ionizing at, or above, a specific energy value, giving rise, in the first instance in the present work, to the M**/HO2 transition. The second anodic peak then relates to slightly less active atoms (M*) capable of yielding HO1 species. At any instant there may be a wide range of surface metal atom activities, the energy level of any one atom varying with its environment (terrace, ledge and kink sites, cluster size, etc.). The active redox responses are assumed to be influenced not only by the state of the metal atoms (M** and M*) but also by the oxide species involved in the oxidation process (HO2 and HO1). As outlined recently for platinum [38], the number of active state transitions may be more extensive than those outlined here. The dynamic character of a metal surface during the course of catalytic processes was highlighted recently by van Oertzen and co-workers [36]. The IHOAM model is based on a similar assumption, i.e. surface metal atoms at active sites are not fixed in a rigid array and are thus capable of participating directly (in a cyclic redox mode which involves atomic motion) in interfacial electrocatalytic processes.

The redox behaviour of palladium single crystal electrodes in acid solution was described recently by Hoshi and co-workers [39]. A notable feature was the appearance in some instances of the reversible transition at 0.25 V (occasionally in combination with a second transition at ca. 0.33 V). The peak at 0.25 V was attributed to anion (HSO_4^- and SO_4^{2-}) adsorption behaviour. This is questionable as the response involved is readily observed [11] with activated polycrystalline palladium surfaces and correlates quite well with multilayer HO2 oxide reduction behaviour (the HO2 oxide is usually assumed [5] to contain solution anions). Since HO2 species can exist in multilayer form, its formation (even at a submonolayer level) cannot be regarded as an adsorption process. Recent work by Kolb and co-workers [31] raises questions as to the application of severe thermal pretreatment (1300 °C in the case of Pd [39]) as a means of producing well-ordered surfaces. Low levels of defect, active surface states are probably very difficult to avoid or eliminate; in our view they are primarily responsible for both premonolayer oxidation phenomena and those electrocatalytic processes which occur in the double layer region.

The most convincing evidence for premonolayer oxidation behaviour of palladium electrodes in acid solution in the present work are the responses recorded at elevated temperatures (Figs. 4, 5, 6). As discussed here earlier, the anodic peak potentials correlate with both multilayer hydrous oxide reduction and electrocatalytic responses; hence a major involvement of redox active impurity species is considered unlikely. The role of absorbed hydrogen (as a source of anodic current) is also largely ignored. The lowest potential used in most of the present work was 0.15 V and this was applied for a period of 3 min in the case of the experiment outlined in Fig. 3b. Since there was no major anodic response in the subsequent anodic sweep, very little hydrogen is absorbed by the metal at $E \geq 0.15$ V. There is no difficulty in cathodically gener-

ating palladium hydride; the metal is simply polarized [24] at $E <$ ca. 0.05 V. When such a PdH_x electrode is subjected to a voltammetric sweep, large, transport-limited, hydrogen oxidation currents were observed, the current values exhibiting a smooth decay and not the type of anodic peaks shown for instance in Fig. 4b. We regard the role of absorbed hydrogen in the present work as being minimal.

Conclusions

1. Palladium, like platinum and gold, in aqueous media exhibits anomalous electrochemical behaviour (or thermodynamically forbidden redox transitions) involving interconversions of active states of surface metal atoms and hydrous oxide species. In an earlier investigation of the palladium system, involving electrochemical activation of the metal surface [11], only one type of active state response (the reversible feature at ca. 0.24 V at 25 °C) was observed. In the present case, using thermal activation, an additional redox response at $E \geq$ ca. 0.45 V was observed in aqueous acid media. The anodic peak in the double layer region (the dashed line in Fig. 6b) indicates that the same transition occurs with Pd in base at room temperature. These anomalous responses with solutions of low pH were significantly enhanced by raising the cell operating temperature.

2. As expected for two metals in the same group in the Periodic Table, the anomalous behaviour of palladium is rather similar to that of platinum. The study of active surface states in general is complicated by the fact that such states are both ill-defined and unstable. For reasons that are as yet unclear, the premonolayer oxidation response for Pd, unlike Pt, often appeared to involve HO1, rather than HO2, formation. Correlations are also pointed out between the active state behaviour of palladium and earlier work on the electrocatalytic properties of this electrode system.

3. In general, active state behaviour of noble metals has been widely ignored in electrochemistry; however, such states are well established in metallurgy [40], where it is accepted that metals can store excess energy via extended defect creation. The study of the electrochemistry of such states at surfaces is difficult as they are usually ill-defined and intrinsically unstable; however, such non-equilibrium states often seem to be the vital active state components in catalysis at surfaces and interfaces.

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